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O. F. Raper

W. B. DeMore

jpl

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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O. F. RAPER AND W. B. DEMORE

*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103*

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The photolysis of O_3 in liquid CO at 77°K has been studied with 2537-Å radiation. Carbon dioxide is formed with a quantum yield of 0.07 and in a 1:1 ratio with O_3 disappearance. The CO_2 quantum yield is reduced by addition of N_2, O_2, or Ar, but is increased by lowering the temperature of the solution.

Formation of CO_2 is attributed to the reaction

$$O(^1D) + CO(+M) \rightarrow CO_2(+M),$$
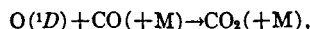
and the low quantum yield is believed to be caused by the reaction

$$O(^1D) + CO + M \rightarrow CO + O(^3P) + M$$
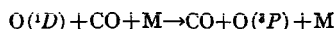
which leads to O_3 reformation. The reaction of O(^1D) with CO is an example of an association process in which the excited association complex may undergo unimolecular decomposition to products of lower electronic energy in the course of stepwise vibrational deactivation. Formation of the association product is of higher order than one with respect to M, the actual order depending on the number of vibrational states in which unimolecular dissociation competes with collisional deactivation. Because of the high-order dependence on M, the rate of product formation is very sensitive to the deactivation efficiency of the third body. The effect of added diluents is believed to arise partly from competition of the added diluents for O(^1D) and partly from the resulting change in solvent deactivation efficiency. The effect of reduced temperature is attributed to an increased rate of deactivation resulting from an increased solvent density.

author

INTRODUCTION

EXISTING information on the O(^1D)–CO reaction has been obtained largely by photolysis of O_2–CO mixtures in the Schumann–Runge region, below 1750 Å, where O_2 absorbs most of the light and dissociates to give O(^3P) and O(^1D). In studies of this type, Jackson[1] and Groth[2] did not observe CO_2 formation at a rate significantly greater than would be estimated on the basis of the recently measured[3-5] rate constant for the reaction O(^3P)+CO→CO_2. On the other hand, Popov[6] reported evidence that O(^1D) reacts with CO much more rapidly than does O(^3P), largely on the walls. Thus there is no evidence that the termolecular reaction

$$O(^1D) + CO + M \rightarrow CO_2 + M \qquad (1)$$

is fast compared to reactions such as O(^3P)+O_2+M→O_2+M and O(^3P)+CO→CO_2, although from the results of Popov, and on general grounds, the reactivity of O(^1D) towards CO is expected to be high.

We have studied the reaction of O(^1D) with CO by ultraviolet (2537-Å) photolysis of dilute O_3–CO solutions at 77°K, using a method similar to that of a recent study of the O(^1D)–N_2 reaction.[7] The results indicate that Reaction (1) is inefficient and that the major reaction is

$$O(^1D) + CO + M \rightarrow CO + O(^3P) + M. \qquad (2)$$
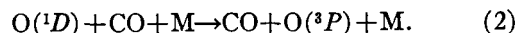
EXPERIMENTAL

Reagents

Ozone was prepared by Tesla coil discharge in O_2 and stored at 77°K. Residual O_2 was removed by pumping to a high vacuum at 77°K and by distilling and collecting in a U-tube at 77°K while pumping. Matheson cp grade CO and Linde high-purity dry N_2 were used; O_2 and Ar were Linde tank grade. In each case the gases were passed through a Drierite–Ascarite column and further purified by two distillations from the liquid, taking the center fraction in each case.

Apparatus

The photolysis cell and light source have been described in the preceding article.[8] The spectrophotometric determination of ozone and mass spectrometric determination of CO_2 (also N_2O) were similar to the previously described methods. The mass spectrometric analyses of CO_2–N_2O product mixtures were based on the m/e 22 peak of CO_2 and the m/e 30 peak of N_2O.

[1] W. F. Jackson, J. Am. Chem. Soc. **56**, 2631 (1934).
[2] W. Groth, Z. Physik. Chem. **37B**, 315 (1937).
[3] B. H. Mahan and R. B. Solo, J. Chem. Phys. **37**, 2669 (1962).
[4] V. N. Kondrat'ev and I. I. Ptichkin, Kinetika i Kataliz **2**, 492 (1961).
[5] L. I. Avramenko and R. V. Kolesnikova, Bull. Acad. Sci. USSR **1959**, 1506.
[6] B. Popov, Acta Physicochim. **3**, 223 (1935).
[7] W. DeMore and O. F. Raper, J. Chem. Phys. **37**, 2048 (1962).
[8] O. F. Raper and W. B. DeMore, J. Chem. Phys. **40**, 1047 (1964).

TABLE I. Rates of O_3 photolysis.

Irradiation time (min)	Ozone concentration ($M \times 10^3$)		Average % absorption[a]	Rate of ozone disappearance (M min$^{-1} \times 10^3$)
	Before	After		
		O_3–CO		
2	0.878	0.756	99.6	0.0612
2	0.756	0.632	99.0	0.0626
2	0.632	0.514	97.8	0.0603
2	0.514	0.398	95.1	0.0610
				0.0612 av.
		O_3–N_2 (Actinometer)		
5	0.944	0.869	99.8	0.0152
5	0.869	0.790	99.7	0.0156
5	0.790	0.715	99.5	0.0151
5	0.715	0.639	99.1	0.0153
				0.0153 av.

[a] Estimated graphically.

Method

The required amount of ozone was first condensed into the cell at 77°K by distillation from an argon bath (87.5°K). The diluent (if any) and CO solvent were then condensed into the cell by distillation from calibrated vessels so that the quantity of each could be determined. The solution was stirred by shaking and then subjected to a succession of short irradiation periods, monitoring the O_3 concentration spectrophotometrically. Where necessary, a correction was made for incomplete light absorption by O_3.

Since it was found that liquid mixtures of O_3, CO_2, and CO cannot be separated without occasional spurious reaction of O_3 and CO, all remaining O_3 was photolyzed in each experiment before separation of products. Product separation was accomplished by pumping off the solvent at 77°K, followed by vacuum transfer of products from the cell to a sealoff tube fitted with a breakoff seal.

Nonphotochemical reaction between O_3 and CO in solution did not occur at any detectable rate, and blank experiments without O_3 produced CO_2 in amounts less than 5% of the yield of a typical experiment.

Determination of Quantum Yields

Two identical cells were employed for quantum yield determinations, one containing the test solution and the other containing an actinometric solution. The primary actinometer was a 5:1 oxalic acid–uranyl oxalate mixture.[9] On the basis of the primary actinometer, the

[9] W. A. Noyes and P. A. Leighton, *The Photochemistry of Gases* (Reinhold Publishing Corporation, New York, 1941), p. 83.

quantum yield for O_3 photolysis in liquid N_2 at 77°K was found to be 0.018, in good agreement with previous results.[7] The O_3–N_2 solution was then used as a secondary actinometer, since the quantum yield was found to be independent of O_3 concentration in the range used and the rate of O_3 photolysis could be conveniently measured spectrophotometrically. By alternately irradiating the test solution and the secondary actinometric solution, the quantum yield of O_3 photolysis could then be calculated from the relative rates of O_3 consumption in the two cells.

The O_3 extinction coefficients have been measured in several low temperature solvents,[10] the values used in this work were 3030 liter mole^{-1} cm^{-1} for O_3 in CO and 3120 liter mole^{-1} cm^{-1} for O_3 in N_2, both at 2537 Å and at 77°K.

Nitrous oxide is recovered in only 94% yield on the basis of O_3 decomposed in these experiments. The reason for the N_2O loss is not known, but the loss is independent of the amount of N_2O present over the range used, and therefore all N_2O yields were corrected by this factor.

RESULTS

Irradiation of O_3–CO Mixtures

Table I shows the results of irradiating an O_3–CO solution and the actinometric O_3–N_2 solution. In neither case is there evidence of dependence of the photolysis rate on O_3 concentration. The rate of O_3 disappearance in the O_3–CO solution is four times that in the O_3–N_2 solution, and since the quantum yield of O_3 disappearance in N_2 is 0.018, the quantum yield in CO is 0.072.

The first three rows of data in Table II show the stoichiometric relationship between CO_2 produced and O_3 destroyed in the photolysis of O_3–CO mixtures. The results correspond within experimental error to the over-all reaction

$$O_3 + CO \overset{h\nu}{\longrightarrow} O_2 + CO_2. \tag{3}$$
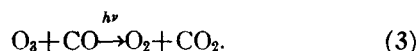
Since the photolysis rate is not dependent on O_3 concentration, and since CO_2 is formed stoichiometrically, the reaction

$$O(^1D) + O_3 \rightarrow 2O_2, \tag{4}$$

does not occur to a significant extent under the conditions of these experiments.

Effect of Added N_2, O_2, and Ar

The diluents N_2, O_2, and Ar were added to the O_3 mixtures to determine their effects on the quantum yields. In the case of N_2 an additional path for O_3 loss

[10] W. B. DeMore and O. F. Raper (to be published).

TABLE II. Product yields and the effect of added nitrogen.

Mixture (mole fractions)			Products (moles$\times 10^7$)			Ozone decomposed (moles$\times 10^7$)		
CO	N$_2$	Φ(O$_3$)	CO$_2$	N$_2$O	Total		Φ(CO$_2$)	Φ(N$_2$O)
1.000	...		26.3		26.3	26.0		
1.000	...		35.8		35.8	34.9		
1.000	...	0.072	22.6		22.6	21.5		
0.814	0.186	0.0617	19.8	2.31	22.1	22.3	0.0553	0.0064
0.684	0.316	0.0541	14.4	3.44	17.8	18.1	0.0438	0.0103
0.515	0.485	0.0435	14.9	6.86	21.8	21.8	0.0298	0.0137
0.352	0.648	0.0368	7.54	6.50	14.0	14.1	0.0198	0.0170
0.250	0.750	0.0314	5.82	7.05	12.9	12.7	0.0142	0.0172
0.178	0.822	0.0261	4.54	8.77	13.3	13.3	0.0089	0.0172
0.171	0.829	0.0271						
0.096	0.904	0.0240	5.54	17.0	22.5	22.6	0.0059	0.0181
...	1.000	0.0180						

is available by means of the photochemical reaction,[7]

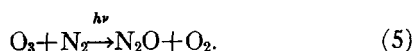$$O_3 + N_2 \xrightarrow{h\nu} N_2O + O_2. \qquad (5)$$

Table II lists the quantum yields of O$_3$ disappearance and the quantum yields of CO$_2$ and N$_2$O formation for several O$_3$–CO–N$_2$ solutions. In each case the ratio of O$_3$ decomposed to products formed is found to be 1:1.

As shown by the data of Table III, dilution of O$_3$–CO mixtures with argon lowers the quantum yield of O$_3$ photolysis (and therefore CO$_2$ formation) by a significant amount, whereas comparable dilution of O$_3$–N$_2$ mixtures with argon[7] had no observable effect on the N$_2$O quantum yield.

The effect of added O$_2$ on the CO$_2$ quantum yield is complicated by the fact that O$_3$ and CO$_2$ are formed

TABLE III. Effect of added argon.

Mixture (mole fractions)		
CO	Ar	Φ(O$_3$)
1.000	...	0.072
0.867	0.133	0.0613
0.757	0.243	0.0543
0.676	0.324	0.0473
0.620	0.380	0.0434
0.595	0.405	0.0440
0.564	0.436	0.0406

by a photochemical O$_2$–CO reaction.[8] However, the data of Ref. 8 allows separation of the two processes and the results for added O$_2$ are shown in Fig. 5 of that paper.

Temperature Dependence of the Quantum Yields

The temperature dependence of the quantum yield was determined in a qualitative manner by pumping on the liquid-N$_2$ coolant, which lowered the temperature of the photolysis solutions by ten or more degrees. In an O$_3$–CO solution the rate of O$_3$ photolysis, and therefore the CO$_2$ quantum yield, was increased by 10% upon cooling. Similarly, the rate of O$_3$ photolysis was increased 18% upon cooling an O$_3$–N$_2$ solution.

DISCUSSION

The question of the identity of the reactive species in experiments involving ultraviolet photolysis of O$_3$ has been discussed previously,[7,11,12] and there is considerable evidence that in experiments such as the present the chemical effects are due to reaction of O(^1D). Although the possibility of excited O$_3$ reactions cannot be rigorously excluded, we shall assume in the following discussion that O(^1D) is the important reactive species.
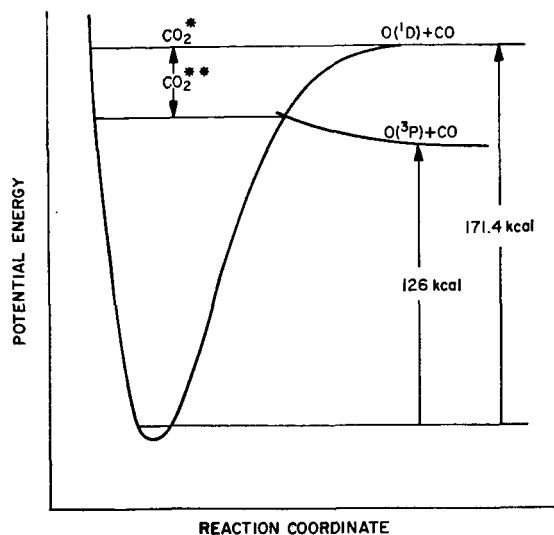
The principal experimental result of this work is the low-quantum yield observed for CO$_2$ formation. This result could be explained in several ways: (1) a low quantum yield of O(^1D) production, (2) loss of O(^1D) by side reactions, or (3) electronic deactivation of

[11] H. Taube, Trans. Faraday Soc. **53**, 656 (1957).
[12] D. Katakis and H. Taube, J. Chem. Phys. **36**, 416 (1962).

FIG. 1. Schematic diagram of CO_2 potential curves.

anism in the present case is as follows:

$$O_3+h\nu\rightarrow O_2+O(^1D), \qquad (6)$$

$$O(^1D)+CO\rightleftharpoons CO_2^*, \qquad (7, 8)$$

$$CO_2^*+M\rightarrow CO_2^{**}+M, \qquad (9)$$

$$CO_2^{**}+M\rightarrow CO_2+M, \qquad (10)$$

$$CO_2^{**}\rightarrow CO+O(^3P), \qquad (11)$$

$$O(^3P)+O_2\rightarrow O_3. \qquad (12)$$

As shown in Fig. 1, which illustrates the CO_2 potential curves schematically, CO_2^{**} represents an excited CO_2 which may have suffered partial vibrational deactivation by the solvent, but still lies in the energy region where dissociation to $CO+O(^3P)$ is energetically possible. Assuming that the quantum yield of $O(^1D)$ formation is approximately unity, the observed

$O(^1D)$ to the ground state $O(^3P)$, the latter species being capable only of O_3 regeneration by reaction with O_2. Of these possibilities, No. (3) is most probable, for the following reasons.
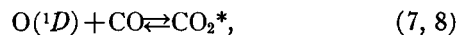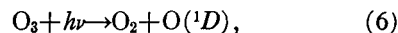
There is evidence that the quantum yield of $O(^1D)$ production in the initial step of O_3 photolysis is high, possibly near unity, based on exchange experiments and on the wavelength dependence of O_3 photolysis.[7] In addition, Taube[11] has obtained quantum yields as high as 0.6 in a photolytic reaction of O_3 believed to require $O(^1D)$ formation.

Loss of $O(^1D)$ by reaction with O_3 has been shown to be negligible; in fact, the principal advantage of O_3 photolysis in solution is that slow, high-order reactions of $O(^1D)$ with the solvent can compete with bimolecular reactions which overshadow them in the gas phase. Reaction of $O(^1D)$ with O_2 impurity can also be ruled out on the basis of the observed effect of added O_2.
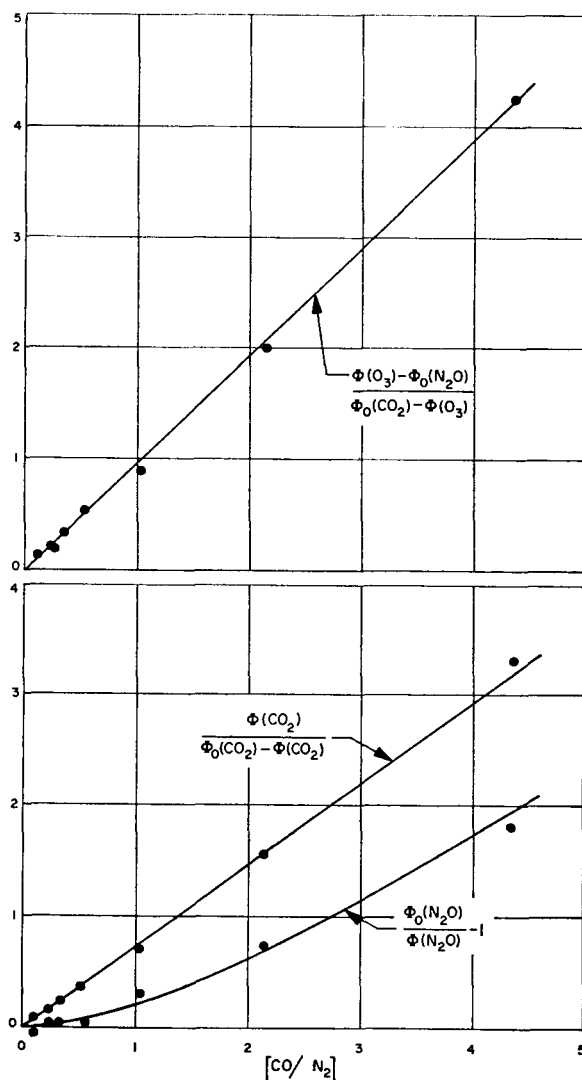
It thus appears that the major loss of $O(^1D)$ is by deactivation to the ground state. Electronic deactivation of $O(^1D)$ by CO, although spin forbidden, is not expected to be inefficient because there is a possibility of transfer from a singlet potential surface of $O(^1D)$–CO interaction to a triplet surface of $O(^3P)$–CO interaction.

The reaction of $O(^1D)$ with CO, and the previously studied $O(^1D)$–N_2 reaction, are examples of a type of association process in which the initial excited association complex may not only redissociate to the original reactants, in the absence of third-body deactivation, but also is unstable with respect to predissociation to products of lower electronic energy. Also, predissociation may occur at a number of stages in the over-all process of vibrational deactivation. The detailed mech-

FIG. 2. Quantum yields in O_3–CO–N_2 mixtures.

CO_2 quantum yield of 0.07 shows that predissociation occurs about 15 times faster than deactivation to CO_2.

Association reactions of this type are of higher order than one with respect to the third body M.[13] The actual order depends on the number of vibrational states available to CO_2^{**} in which predissociation (a unimolecular process) competes with deactivation (first order in M). The rate of CO_2 formation is given, approximately, by

$$\frac{d(CO_2)}{dt} = \left(\frac{k_9[M]}{k_{11}+k_9[M]}\right)^{n-1}\frac{k_9 k_7[O^1D][CO][M]}{(k_8+k_{11}+k_9[M])}, \quad (13)$$

where n is the average number of vibrational states having $k_{11} \neq 0$ through which CO_2^{**} passes. A more detailed treatment would include a dependence of k_9 and k_{11} on the vibrational states, and would also take into account the possibility of several different deactivation paths.

In view of the foregoing results, the predissociation reaction may be expected to predominate in the gas phase, so that the major reaction in that case will be either Reaction (2) or the bimolecular reaction

$$O(^1D)+CO \rightarrow O(^3P)+CO. \quad (14)$$
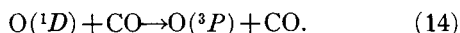
Reaction (14), which involves CO_2^* as an intermediate, would have a rate constant equal to $k_7 k_{11}/(k_8+k_{11})$ in the limit of low M concentration.

In mixtures of CO and N_2 $O(^1D)$ is removed at a rate given by

$$-d \ln O(^1D)/dt = k_{CO}[CO]+k_{N_2}[N_2], \quad (15)$$

where $k_{CO}=k_7(k_9[M]+k_{11})/(k_9[M]+k_{11}+k_8)$ and a similar expression holds for k_{N_2}. On the basis of a mechanism in which it is assumed that the effective third-body concentration [M] is independent of mixture composition, the following relationships result:

$$\frac{\Phi(O_3)-\Phi_0 N_2 O}{\Phi_0(CO_2)-\Phi(O_3)} = \frac{\Phi(CO_2)}{\Phi_0(CO_2)-\Phi(CO_2)}$$

$$= \frac{\Phi_0(N_2 O)}{\Phi(N_2 O)}-1 = \frac{k_{CO}[CO]}{k_{N_2}[N_2]}. \quad (16)$$

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[13] W. B. DeMore and O. F. Raper, Jet Propulsion Laboratory, Space Programs Summary No. 37–21, Vol. IV, p. 245.

In this expression $\Phi(O_3)$ represents the O_3 quantum yield in a given O_3–N_2–CO solution, $\Phi(N_2 O)$ and $\Phi(CO_2)$ the $N_2 O$ and CO_2 quantum yields in that same solution, and $\Phi_0(N_2 O)$ and $\Phi_0(CO_2)$ the quantum yields for $N_2 O$ and CO_2 in pure N_2–O_3 solutions and pure CO–O_3 solutions, respectively. Figure 2, which is a plot of the data of Table II according to Eqs. (16), shows that a mechanism based only on competition between N_2 and CO for $O(^1D)$ is inadequate to explain the individual quantum yields in the O_3–N_2–CO mixtures. The slopes of the three curves are not equal, as predicted by the mechanism, and some curvature is apparent in the $N_2 O$ plot.

The explanation for the above effects is most likely to be found in the fact that the efficiencies of $N_2 O$ and CO_2 formation are critically dependent on the rates of deactivation of the excited association complexes, as shown by Eq. (13). The effect of a small change in the effective [M] is amplified as a consequence of being raised to the nth power. Thus the addition of N_2 to an O_3–CO mixture not only removes some of the $O(^1D)$ otherwise available to CO, but also may alter the fraction of CO_2^{**} which is deactivated to CO_2. From the appearance of the $N_2 O$ curve in Fig. 2, addition of CO to an N_2 solution seems to increase the efficiency of deactivation of $N_2 O^{**}$.

The fact that lowering the temperature increases the $N_2 O$ and CO_2 yields is consistent with the proposed solvent effect, since the accompanying density increase presumably increases the deactivation rate.

Although solvent effects such as the above preclude quantitative evaluation of the ratio k_{CO}/k_{N_2} in (16), the data of Fig. 2 nevertheless suggests that N_2 and CO are of similar reactivity toward $O(^1D)$. This interpretation is supported by the fact that the effect of adding O_2 to the O_3–N_2 system is only about one magnitude greater than the effect of adding O_2 to O_3–CO mixtures.

The effect of added argon in reducing the CO_2 quantum yield in O_3–CO mixtures, but not the $N_2 O$ quantum yield in O_3–N_2 mixtures, must be ascribed largely to the solvent effect, since it is believed that argon does not deactivate $O(^1D)$ at a rate sufficient to compete with chemical reaction with the solvents N_2 and CO.